Thermal ionization energy of Mg acceptors in GaN: Effects of doping level and compensation

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ABSTRACT

It is shown that the thermal ionization energy of Mg acceptors in GaN, as determined by temperature dependent Hall effect measurements, exhibits the usual dependence on the concentration of ionized impurities, as seen in many other semiconductors. The observed difference in the thermal and optical ionization energies of Mg acceptors can be quantitatively understood based on a simple electrostatic interaction model.

Keywords: thermal ionization energy, gallium nitride (GaN), Mg acceptors.

1. INTRODUCTION

Gallium nitride (GaN) is a promising direct wide band gap semiconductor for potential applications in visible and near-UV optoelectronics and in high temperature electronic devices (for recent reviews see e.g. references[1-4]). In fact the invention of blue semiconductor lasers made from gallium nitride has been one of the key technological breakthroughs of the decade. One of the key steps forward in the long way to the realization of these promises was the achievement of controlled p-type doping using Mg as an acceptor by Amano et al.[5] and later by Nakamura et al.[6] One of the basic characteristics of an acceptor dopant is its ionization energy. The ionization energy of the Mg acceptor as determined by optical (low temperature photoluminescence) methods is 224±4 meV.[7] However reported values of thermal ionization energies for the Mg acceptor are considerably lower, with values scattered in the range from 125 meV to 170 meV based on temperature dependent Hall effect measurements (see e.g. reference[3]), and about 155 to 165 meV based on the temperature dependence of the intensity of donor-acceptor pair emission.[8,9] These large differences are usually ascribed to the ubiquitous concentration dependence of the thermal ionization energy of impurity centres in semiconductors, however, up to now a systematic quantitative analysis has not yet been attempted. For device applications, however, the thermal ionization energy of the dopant is the relevant parameter, because it controls the degree of ionization of the dopant centres, and in this way it determines the available free charge carrier density, dopant efficiency, etc. Because of this it is important to understand these significant differences.

Here I present a quantitative analysis and interpretation of the observed differences in the thermal and optical ionization energies of Mg acceptors in GaN on the basis of the available models for the concentration and compensation degree dependence of thermal ionization energies of impurity centres. It is proposed that these differences can be satisfactorily described using a simple electrostatic interaction model originally due to Pearson and Bardeen[10] and Debye and Conwell,[11] and later discussed and generalized by Monecke et al.,[12] and by the present author.[13-15]

2. MODELS FOR THE CONCENTRATION DEPENDENCE OF THE THERMAL IONIZATION ENERGY

Since the pioneering work of Pearson and Bardeen[10] it has been well known that the thermal activation energy of the impurities decreases with increasing concentration of the impurity centres. Various models[10-12,15] lead to the following generic expression for the dependence of the thermal ionization energy on the majority impurity concentration (acceptors in p-type materials, to be definitive) and on the compensation degree:

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$$E_A = E_A(N_A,K) = E_{Ao} - f(K)\frac{e^2}{4\pi\varepsilon_r\varepsilon_o} N_A^{1/3} \quad (1)$$

here E_{Ao} is the ionization energy of acceptors at infinite dilution, N_A is the acceptor concentration, K is the compensation degree ($K = N_D/N_A$), ε_o is the dielectric permittivity of the vacuum, and ε_r is the static dielectric constant of the host semiconductor. f(K) is a (dimensionless) function, the exact form of which depends on the details of the concrete mechanism leading to the reduction of the thermal ionization energy. E_{Ao} can be identified with the optical ionization energy as determined e. g. from PL measurements.

Several theoretical models are supporting the form of the dependence of E_A on various parameters especially on N_A and K as given by Eq. (1). These include among others the model based on the concept of electrostatic interaction between the free carriers and the oppositely charged impurity centres originally proposed by Pearson and Bardeen[10] and modified by Debye and Conwell,[11] a similar model incorporating also the effects of the relaxation of the distribution of carriers on the impurity centres due to Monecke et al.,[12] and another model based on the concept of random potential fluctuations and quantum overlap effects changing the energy spectrum of impurities, proposed by Lien and Shklovskii[16] (see also references[17,18]). All lead to Eq. (1) but with different functional forms of f(K). Notably, according to Pearson and Bardeen[10] f(K) = 1, according to Debye and Conwell[11] $f(K) = 1.646(4\pi/3)^{1/3} = 2.6533K^{1/3}$, according to Monecke et al.[12] $f(K) = \Gamma(2/3)(4\pi/3)^{1/3} = 2.1828K^{1/3}$, and according to Lien and Shklovskii[16] f(K) is a more complicated function with the value of 1 at K = 0, the value increasing slowly up to about 1.4 for K = 0.4 - 0.6, and dropping more sharply for K > 0.8, and even changing sign above K = 0.93.

3. ANALYSIS OF THE HALL DATA ON p-GaN:Mg AND DISCUSSION

Using the Hall data for GaN:Mg collected from references[19-28] I calculated $f(K)_{exp}$ i.e. the "experimental" values of the function in Eq. (1) for various samples. In order to have a meaningful comparison the hole concentration versus reciprocal temperature curves were reanalyzed using the standard partially compensated single acceptor model:

$$\frac{p(p + N_D)}{N_A - N_A - p} = \frac{1}{\beta} N_V \exp\left(-\frac{E_A}{kT}\right) \quad (2)$$

with $N_V = 4.829\times10^{15}(m^*/m_o)^{3/2}T^{3/2}$. The adjustable parameters were the acceptor concentration N_A, the donor concentration N_D, and the thermal ionization energy of the acceptors E_A. The values used for the constants were as follows: for the impurity level spin degeneracy ß, a value of 4 was chosen, and the density-of-states effective mass of holes in the valence band was assumed to be $m^*/m_o = 0.8$.

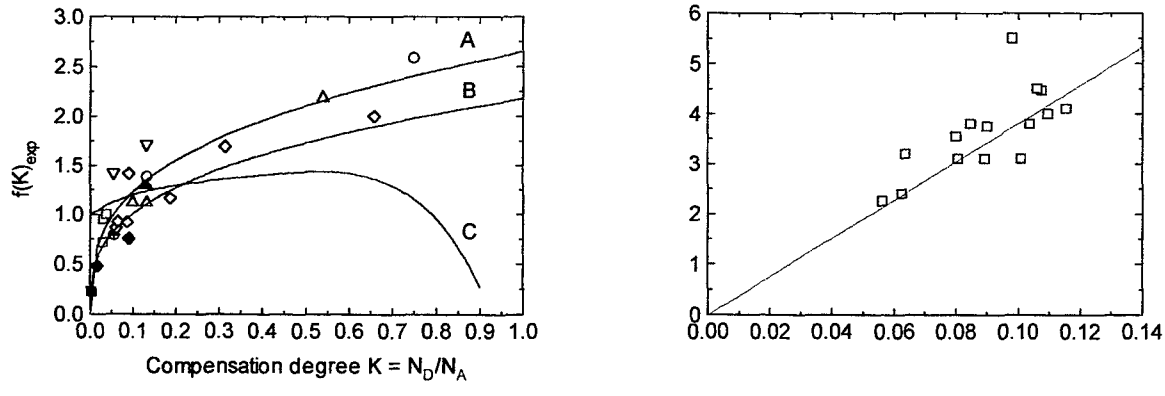

Fig. 1. Theoretical and "experimental" curves of the function f(K) versus K. Data collected and reanalyzed from the literature.[19-27] Theoretical curves: A - according to Debye and Conwell,[11] B - according to Monecke et al.,[12] C - according to Lien and Shklovskii.[16]

Fig. 2. Plot of the values of α versus the reciprocal dielectric constant for various semiconductors. The straight line corresponds to $\alpha\varepsilon_r = 38.2\text{x}10^{-5}$ meVcm. Data and plot from Pődör,[13,14] the GaN datum point is the present result.

The results obtained for f(K) versus K are presented in Fig. 1 together with the theoretical curves for the models of Debye and Conwell,[11] Monecke at al.,[12] and Lien and Shklovskii.[16] In evaluating f(K) from Eq. (1) the acceptor ionization energy at infinite dilution was taken as $E_{Ao} = 224$ meV, and the relative dielectric constant as $\varepsilon_r = 9.6$. Notwithstanding the relatively big scatter, the data follow a common trend, i. e. the values of $f(K)_{exp}$ deduced from the Hall curves reported in the literature increase monotonously with increasing K, and the actual values of the function $f(K)_{exp}$ seem to be somewhat better described by the model due to Debye and Conwell[11] than by the model of Monecke et al.,[13] without any fitting parameter. It is to be noted that in the limit of K = 0 the deduced values of $f(K)_{exp}$ tend to zero. The theoretical curve based on the model of Lien and Shklovskii[16] is clearly at variance with the data analysed here. In the range of intermediate compensation (K = 0.3 to 0.6) the values of $f(K)_{exp}$ lie significantly higher than the curve corresponding to this model, and at high compensation degrees this difference reaches a factor of 2 to 3. Similar behaviour of the function f(K) in various semiconductor-impurity systems has already been noted by Zabrodskii and Timofeev[18] and by the present author[15] too.

If we suppose the *a priori* applicability of the electrostatic interaction model of Debye and Conwell to the experimental data, as the validity of this assumption is being corroborated by the results of analysis of a great amount of data,[10-14] then using the relationship $N_D = KN_A$ Eq. (1) can be rewritten as

$$E_A = E_{Ao} - 2.6533\frac{e^2}{4\pi\varepsilon_r\varepsilon_o}N_D^{1/3} = E_{Ao} - \alpha N_D^{1/3} \qquad (3)$$

with a theoretical value of $\alpha = 38.2\text{x}10^{-5}/\varepsilon_r$ (meVcm). Using the model of Monecke et al.[12] the constant would be $\alpha = 31.4\text{x}10^{-5}/\varepsilon_r$ (meVcm).

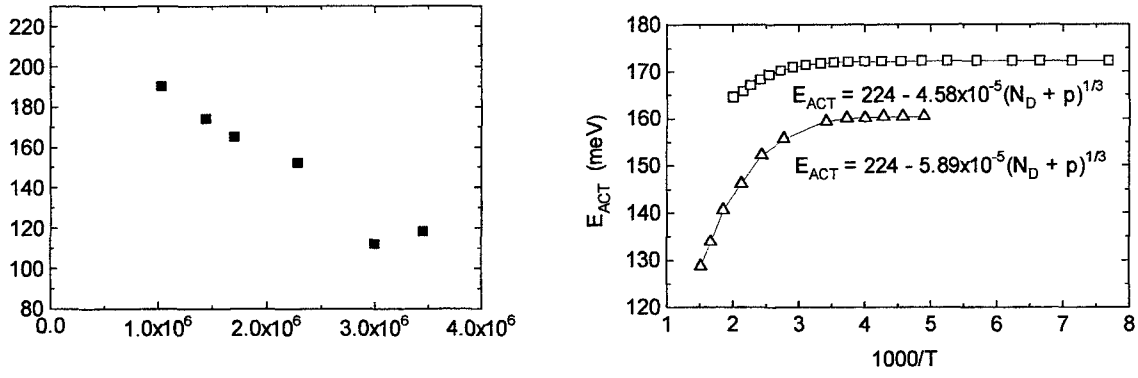

Fig. 3. Plot of the thermal activation energy of Mg acceptors in GaN versus the cubic root of the compensating impurity (donor) concentration. Up triangles, solid circles, down triangles, squares, circles, solid squares - data from the literature.[19,21,22,26,27,28] The straight line represents the least-squares fit to the data.
Fig.4. Acceptor activation energies deduced using a model incorporating the dependence of the activation energy on the concentration of ionized acceptors: $N_{Ai} = N_D + p$. Triangles - data from Nakayama et al.,[21] squares - data from Götz et al.,[23] reanalyzed with $E_{Ao} = 224$ meV.

This model suggests that the value of α for various impurities in the same semiconductor host should be equal, and the values of α for different semiconductors should scale with the reciprocal of the dielectric constants. An analysis of the available large amount of data for group IV, III-V, II-VI and II-IV-V_2 semiconductors confirms this statement.[13,14] Fig. 2, after[13,14] summarizes these results. Empirically it was found that $\alpha = (40\pm5)\text{x}10^{-5}/\varepsilon_r$ meVcm, which corresponds to the theoretical value for the model of Debye and Conwell.[11] Fig. 3. presents the data for GaN:Mg plotted according to Eq.

(2). Least-squares fit yields $E_A = (217 \pm 8) - (3.14 \pm 0.40)\times10^{-5}N_D^{1/3}$ (energy in meV, concentration in cm^{-3}). The energy intercept agrees within error with the optical ionization energy, the fitted value of the slope α however, as can be seen in Fig. 2, is lower than the theoretical value for the model of Debye and Conwell,[11] and is close to that expected for the model of Monecke et al.[12] However, if the fit is performed with a fixed intercept $E_{Ao} = 224$ meV, a greater value of α is obtained, which is close to the value expected on the basis of the model of Debye and Conwell.[11]

The usual interpretation attached to Eq. (3) is that the thermal ionization energy decreases linearly with the cubic root of the ionized acceptor (majority impurities in p-type material) concentration because, at least at low temperatures where $p << N_A$, N_D, $N_{Ai} \approx N_D$. However, in general $N_{Ai} = N_D + p$, therefore in the strict sense of the electrostatic interaction models (like of Debye and Conwell[11] and of Monecke et al.[12]) in Eq. (3) $N_{Ai} = N_D + p$ should figure instead of N_D.[29] With this refinement instead of Eq. (3) we have

$$E_A = E_{Ao} - \alpha N_{Ai}^{1/3} = E_{Ao} - \alpha(N_D + p)^{1/3} \tag{4}$$

implying that the "effective" thermal ionization energy itself depends on the temperature through the temperature dependence of the carrier concentration p. Typical results of Hall curve fits, taking into account the implicit temperature dependence of the thermal activation energy as given by Eq. (4), are presented in Fig. 4. In these fits E_{Ao} =224 meV, a constant, was assumed. As might be expected from Eq. (4), the fitted activation energies exhibit a substantial decrease at higher temperatures, and concomitantly and somewhat surprisingly, the fitted values of the constant α are 20-40 per cent higher than those obtained from the conventional analysis, and also from the electrostatic interaction model.[11]

4. CONCLUSIONS

The observed differences in the thermal and optical ionization energies of Mg acceptors in GaN were analyzed on the basis of the available models for the concentration and compensation degree dependence of thermal ionization energies of impurity centres. It was established that these differences can be satisfactorily described using a simple electrostatic interaction model originally due to Pearson and Bardeen and Debye and Conwell.

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